

COAL PYROLYSIS AT HIGH TEMPERATURE*

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INTRODUCTION

This paper considers the application of a recently developed pyrolysis model to the high temperature rapid pyrolysis of coal in an entrained flow reactor. The model is based on experiments using a heated grid pyrolysis apparatus, which have helped to establish a relationship between the chemical structure of a coal and its pyrolysis products (1-9). The relationship has been incorporated into a kinetic model of thermal decomposition (1-6) which has the following general features: 1) The time and temperature dependent evolution of the products of thermal decomposition are predicted using a general set of kinetic parameters and a knowledge of the coal's structural composition; 2) the evolution of a species results from the thermal decomposition of a particular structural element within the coal at a kinetic rate which depends on the type of element but which is relatively insensitive to coal rank; 3) much of the needed structural information can be obtained from quantitative Fourier Transform Infrared (FTIR) analysis of the coal and pyrolysis products. The model has proved successful in simulating the results of vacuum thermal decomposition experiments in a heated grid for a variety of bituminous coals and lignites.

The heated grid experiment has advantages over other pyrolysis experiments in achieving good mass and elemental balances and in allowing the primary pyrolysis products to be observed with minimal secondary reactions. It has the distinct disadvantage, however, that the heating of the coal is slower than in practical devices and it is very difficult to measure or estimate the time-temperature history of the coal. While the general concepts of the thermal decomposition model and the relative magnitude of kinetic rates appear to be valid, the exact kinetic rates especially at high temperatures are uncertain. To improve the kinetic data, other experiments are needed. In one approach which has recently been reported, coal is dropped into a hot furnace and the evolving gases are monitored in-situ with a FTIR (10). This experiment verified the general features of the model but yielded higher kinetic rates. The experiment could only follow events on a time scale longer than a few hundred milliseconds due to the limit imposed by the FTIR scanning rate. Data was presented for temperatures between 500° and 800° C.

In the present investigation, results are extended to temperatures up to 1470° C and higher rates using pyrolysis experiments performed in an entrained flow reactor at Combustion Engineering. In this experiment coal is injected into a hot gas stream and after a variable residence time of 0 to 450 milliseconds, the reaction is quenched. The pyrolysis gas compositions were determined and the chars were analyzed by FTIR, elemental analysis and optical microscopy to determine the changes in char chemistry and physical appearance. The time-temperature histories of the solid particles have been calculated to provide input to the pyrolysis model. The pyrolysis model was successful in simulating the reactor data after adjustment to the kinetic rates at high temperatures.

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EXPERIMENTAL

Combustion Engineering's Drop Tube Furnace System (DTFS) is similar in design to the reactors described by Nsakala et. al. (11) and Badzioch and Hawksley (12). The DTFS (Fig. 1) is comprised of a 2.54 cm inner diameter preheater, a 5.08 cm inner diameter test furnace, a fuel feeding system, and a gas analysis system. Both furnaces are powered with silicon carbide (SiC) heating elements.

The conditions of this particular experiment were as follows follows: 1) A 200 x 400 mesh size fraction of Pittsburgh seam coal was introduced by screw feeding through a water-cooled probe into the test furnace reaction zone; 2) The primary stream (comprised of the fuel fed at a rate of 1 gram/min and 15% CO₂/85% N₂ carrier gas fed at 2 liters/min) was allowed to mix rapidly with a preheated down-flowing secondary gas (15% CO₂/85% N₂) stream (fed at 28 liters/min); 3) After a variable distance (zero to 40.6 cm) the pyrolysis products were aspirated in a water-cooled probe to quench all the reactions; 4) The solids were separated from gaseous products in a small cyclone; 5) A portion of the gas sample was analyzed on-line to determine NO_x, O₂, CO, CO₂ and SO₂ concentrations; and 6) Solid samples were analyzed by FTIR, ultimate analysis and optical microscopy. Experiments were performed with furnace wall temperatures of 1370 and 1470°C. Free fall velocities of particles in these experiments were small compared with gas velocities; hence it was assumed that the particles traveled at the same velocities as the gas. Maximum residence times in the reaction zone varied from 0.342 to 0.453 sec for the higher and lower temperature, respectively.

PYROLYSIS RESULTS

The physical and chemical changes occurring during pyrolysis are characterized by the data illustrated in Figs. 2, 3, 5 and 6. Figure 2 follows the infrared spectra of solid samples collected at various positions in the reactor. The techniques for preparing and analyzing the FTIR spectra have been presented previously (2). The figure presents the absorbance from 1 mg of sample in a KBr pellet or 1 mg/1.33 cm². The data are for a wall temperature of 1370°C. The results indicate that no changes occur for the first 5 cm in the reactor. Between 5 and 10 cm the absorbance in the aliphatic stretch region at 2900 cm⁻¹ decreases, indicating a decreasing concentration of aliphatic C-H bonds which goes to zero at 20 cm. The behavior of the aromatic stretch region at 3050 cm⁻¹ indicates that the aromatic C-H concentration starts to decrease between 10 and 20 cm. The behavior of the region near 1200 cm⁻¹ indicates that the density of O-C bonds is not decreased during the initial stage of pyrolysis. The FTIR spectra for the 1470°C wall temperature are similar except that the aliphatic C-H concentration goes to zero at 10 cm and the aromatic C-H concentration at 10 cm is about the same as it is for 20 cm in the lower temperature run.

The samples were examined optically to determine physical change occurring during pyrolysis. In agreement with the FTIR results, little happens to the samples collected at 5 cm or less. At 10 cm however, the particles are observed to have become substantially swollen. By 20 cm they are well formed structures which look like foamy soap bubbles. The wall thickness in these bubbles appears to be about 1 micron. At 30 and 40 cm the bubbles appear to be more opaque and have shrunk slightly. Results for the 1370°C run showing samples collected at zero and 20 cm are presented in Fig. 3. The long dimension of the photomicrograph is 1.9 mm. The swelling increases the diameter by a factor of about 4.

CALCULATION OF TIME-TEMPERATURE HISTORIES

Calculations were made of the following quantities: 1) the average gas temperatures in the preheater, the experimental section and the collection probe; 2) the radially dependent gas temperature in the experimental section; 3) the coal particle temperatures and 4) the temperature of a thermocouple at positions along the reactor

center line. The calculations include a model for the particle swelling which is found to produce a rapid temperature rise because of the increase in surface area for absorbing radiation.

To determine both radial and longitudinal temperature profiles, calculations were performed numerically on a PDP/11 computer by considering tubular shells at progressive cross sections of the flow path. The radial gas temperatures are calculated for the primary gas core, and for n concentric rings of gas. The total calculation proceeds as follows: starting at the inlet, with the particle temperature set equal to the primary gas temperature, $n-1$ concentric gas rings set equal to the secondary gas temperature, and the outer ring fixed at the wall temperature, a system of differential equations are integrated using a Runge-Kutta integration scheme to determine the temperature of each element at the next time increment. (Note-The differential equations include: a) radiative heat transfer between the coal particles and the wall including the effects of the cold injector and collector; b) convective heat transfer between the coal and the core gas c) conductive heat transfer within the gas; and d) the heat capacities of the coal and gas). Using these new temperatures, an average temperature for the gas is calculated (the temperature after complete mixing), and this average temperature is used to calculate an average velocity, which in turn is used to calculate the axial position of the particles and the gas. The results of the calculations were compared with standard predictions for heat transfer in a pipe (13) and it was found that under the particular conditions of the experiment the additional heat transfer due to convection and turbulence (even in the collection tube) could be neglected. The general conclusion from these calculations is that the particle temperature is dominated by radiation from the hot furnace walls. The particles heat rapidly and achieve temperatures close to the wall temperatures. The local gas around the particles (e.g. the primary gas stream) is heated by conduction from the particles but the secondary gas stream is not well coupled to the particles. For this reason mixing effects appeared to be of minor importance for calculating particle temperatures in the reactor section.

The results of the calculation for the collection probe at 5 and 10 cm are shown in Fig. 4. For the 5 cm case the particle temperature rises rapidly, driven by radiative heating. The primary gas temperature also rises rapidly (much faster than in the absence of the coal) due to heat transfer from the coal. The average gas temperature is dominated by the secondary gas which is not well coupled to the coal particles and thus heats as in the case for no coal. The temperature for the coal and the gas is assumed to fall in the smaller diameter collection probe at a uniform temperature due to turbulent mixing. To cool below reaction temperatures takes about 20 milliseconds.

The particle volume is assumed to increase with the volume of evolved gases until it has reached four times its original diameter, which appeared to be the experimentally observed limit. According to the prediction at the 5 cm collection point the particle diameter starts to change slightly for the higher wall temperature experiment but not for the lower wall temperature. The volatile yield corresponding to this change would be less than 1%. These results are in agreement with the chemical and FTIR measurements of the samples for 5 cm and less which show no measurable change from the raw coal and with the visual observation of the 5 cm sample which shows some slight particle swelling for small particles in the high temperature wall case.

By 10 cm the coal for both wall temperatures has come to within 100 kelvins of the wall temperature. The coal temperature exceeds the average gas temperature because of the better radiation coupling to the wall. The particle swelling is complete for both wall temperatures in agreement with the visual observation of the samples for 10 cm and greater.

PYROLYSIS MODEL

The pyrolysis model assumes a coal structure consisting of highly substituted aromatic ring clusters containing heteroatoms linked by relatively weak aliphatic bridges. Evidence suggests that during thermal decomposition these weak links break, releasing the clusters and attached bridge fragment which comprise the tar. Simultaneous with the evolution of tar molecules is the competitive cracking of bridge fragments, substituted groups and ring clusters to form the light molecular species of the gas. The quantity of each gas species depends on the functional group distribution in the original coal. At low temperatures there is very little rearrangement of the aromatic ring structure. There is, however, decomposition of the substituted groups and aliphatic (or hydroaromatic) structures resulting in CO_2 release from the carboxyl, H_2O from hydroxyl, hydrocarbon gases from aliphatics, H_2S from mercaptans and some HCN and CO from weakly bound nitrogen and oxygen groups. At high temperature there is breaking and rearrangement of the aromatic rings. In this process, H_2 is released from the aromatic hydrogen, CS_2 from the thiophenes, HCN from ring nitrogen and additional CO from tightly bound ether linkages. As this process continues the char becomes more graphitic.

A striking feature of thermal decomposition which was observed for a variety of coals is that the temperature dependent evolution rate of a particular species is similar for all coals. This is true even though the amount of the species may vary substantially from one coal to another. These rates characterize the thermal decomposition of the various functional groups. They depend on the nature of the functional group but appear insensitive to coal rank. The differences between coals may be attributed to differences in the mix of functional groups.

The mathematical description of the pyrolysis model has been presented previously (1-6). The evolution of tar and light species provide two different mechanisms for removal of a functional group from the coal; evolution as a part of a tar molecule and evolution as a distinct species with cracking of the molecule. To model these two paths with one path yielding a product which is similar in composition to the parent coal, the coal is represented as a rectangular area with X and Y dimensions. The Y dimension is divided into fractions according to the chemical composition of the coal. Y_i^0 represents the initial fraction of a particular component (carboxyl, aromatic hydrogen, etc) and $\sum Y_i^0 = 1$. The evolution of each component into the gas (carboxyl into CO_2 , aromatic hydrogen into H_2 , etc) is represented by the first order diminishing of the Y_i dimension, $Y_i = Y_i^0 \exp(-k_i t)$. The X dimension is divided into a potential tar forming fraction X^0 and a non-tar forming fraction $1-X^0$ with the evolution of the tar being represented by the first order diminishing of the X dimension $X = X^0 \exp(-k_t t)$. The amount of a particular component in the char is $(1-X^0+X)Y_i$ and the amounts in the gas and tar may be obtained by integration. In the heated grid experiment the products cool upon evolution so they undergo no further reactions. In the present experiment, the evolved products continue to react. Under these conditions it has been assumed that the decomposition of a component occurs at the same rate in the evolved product as it does in the char.

The coal compositional parameters for the Pittsburgh seam coal and the kinetic rates used in the simulation are presented in Table I. Most of the composition parameters have been obtained from elemental and FTIR analysis. The carboxyl, CO-loose and N-loose have been estimated from the parameters of a previously run Pittsburgh seam coal (5) by assuming that these components represented the same fraction of the oxygen and nitrogen in both coals. The split of the N and CO into loose and tight groups conforms to the experimental observation that these components have at least two distinct evolution rates which presumably indicate distinct chemical species. The tar was estimated from the previously measured coal, but decreased by 30% to

account for the decrease in going from vacuum to 1 atmosphere (see Ref. 9). The kinetic rates have been modified from those most recently presented (5). 1) The H_2 and CO-tight rates have been increased at high temperature to match the new experimental data. 2) The rates for the other species appeared to be adequate at high temperature. However, the recent experiments by Freihaut et al (10) suggest that they are low in the range 500-800°C. The rates of Table I are a compromise between these observations and the heated grid data. 3) The rates have also been simplified by using the same rate for tar, N-loose, CO-loose, carboxyl and hydroxyl instead of 5 slightly different rates.

RESULTS

The theory and experiment are compared in Figs. 5 and 6 for the two temperatures (1370°C and 1470°C) which were measured. Fig. 5a and 5b illustrate the char composition. The model predicts that little happens for the first 5 cm for both temperatures. At 10 cm and longer there are substantial changes especially in the hydrogen and oxygen. The model predicts a rapid decrease in the aliphatic hydrogen followed by a slower decrease in the aromatic hydrogen. This behavior is confirmed by the FTIR spectra. The model prediction for oxygen indicates an initial rapid evolution of CO_2 , H_2O and CO-loose and a slower evolution of CO-tight from ether groups. The FTIR spectra (Fig. 2) show a rapid decrease in the OH concentration indicated by the decrease in the broad peak between 3600 and 2200 cm^{-1} and the sharp peak at 1600 cm^{-1} which is attributed to an aromatic ring stretch enhanced by attached hydroxyl groups (2). (Note- The decrease in the broad band is confused by the persistence of a narrower KBr- H_2O peak at 3400 cm^{-1} . This occurs because much less sample is used for the high carbon content chars so that scaling the spectra to 1 mg/1.33 cm^2 enhances the contribution from the KBr.) As the char oxygen decreases, the CO concentration increases in agreement with the data in Figs. 5c, and 5d. Predictions for CO_2 and H_2O produced in pyrolysis are also presented. These predictions do not include secondary gas-char reactions.

Figures 6a and 6b show predictions for four additional evolved species. The stable products from the evolution of the hydrocarbons are H_2 and soot. This was observed in the heated grid experiments (3,5). The methane and acetylene are predicted to be short lived due to thermal cracking to soot and hydrogen.

Figures 6c and 6d show the overall product distribution. The experimental points are obtained using the ash tracer method (14). Unfortunately, soot may be included in varying amounts with the char. This would tend to underestimate the char concentration by a varying amount.

CONCLUSION

A pyrolysis model which was developed to simulate coal pyrolysis in a heated grid appears to be successful in simulating the high temperature pyrolysis of coal in an entrained flow reactor. The model relates evolved products to the coal structure. The structure parameters for the coal were input on the basis of the parameters obtained for a similar coal in the heated grid. No adjustments of these structure parameters were made in making the simulation. The kinetic parameters were modifications of the parameters derived from the heated grid experiments. Major changes were made in the aromatic hydrogen and CO-tight rates at high temperatures. The exponential and preexponential factors for these two components were adjusted to increase the rate in the range 1370-1470°C but hold its value close to the original rates at lower temperature so that a fit is still obtained for the heated grid data.

The rates for aliphatics, tar, hydroxyl, CO-loose, N-loose and carboxyl received minor adjustments and so still fit the heated grid data.

The rates with the greatest uncertainty are those for olefin, acetylene and soot for which there is no data from the present experiment. The soot rate (the rate for

conversion of aliphatic to soot) is the highest rate in the simulation. It dominates the initial fast change in the coal. Additional experimental work is needed to sort out the effects of the aliphatic evolution and subsequent cracking to olefins, acetylene and soot.

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TABLE I

Kinetic Rates and
Functional Group Composition for a Pittsburgh Seam Bituminous

Composition Parameter (dmmf)	Pittsburgh Seam Bituminous	Kinetic Rates	
C	.853		
H	.057		
N	.017		
S(organic)	.021		
O	.052		
S(mineral)	.014*		
CO ₂ - Carboxyl	.006	k ₁ = 5400	exp (-8850/T)
H ₂ O - 9/17 Hydroxyl	.010	k ₂ = 5400	exp (-8550/T)
CO - Ether Loose	.006	k ₃ = 5400	exp (-8850/T)
CO - Ether Tight	.062	K ₄ = 2.15 x 10 ¹⁶	exp (-57000/T)
N - Nitrogen Loose	.003	k ₅ = 5400	exp (-8850/T)
N - Nitrogen Tight	.014	k ₆ = 290	exp (-13000/T)
CH _{1.8} - Aliphatic	.276	k ₇ = 19000	exp (-11000/T)
H _{1.8} - Aromatic H	.020	K ₈ = 40644	exp (-14085/T)
C - Non Volatile	.582	K ₉ = 0	
S - Organic	.021		
Total	1.000		
Tar	.30	K _t = 5400	exp (-8850/T)
Olefins		K _o = 2 x 10 ⁹	exp (-24000/T)
Acetylene		K _a = 1 x 10 ¹⁶	exp (-50000/T)
Soot		K _s = 4 x 10 ¹⁹	exp (-60000/T)

*Dry

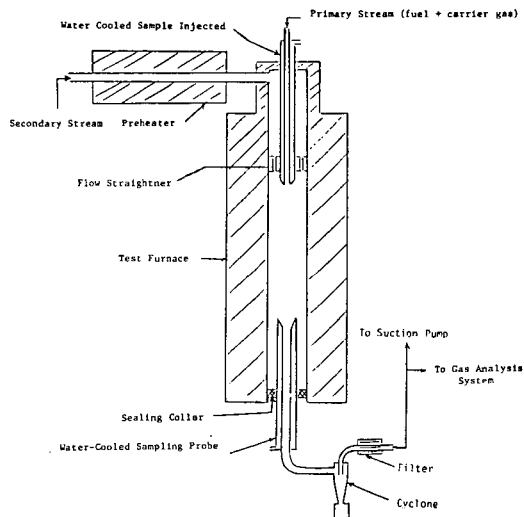


FIGURE 1 SCHEMATIC OF THE COMBUSTION ENGINEERING DROP TUBE FURNACE SYSTEM.

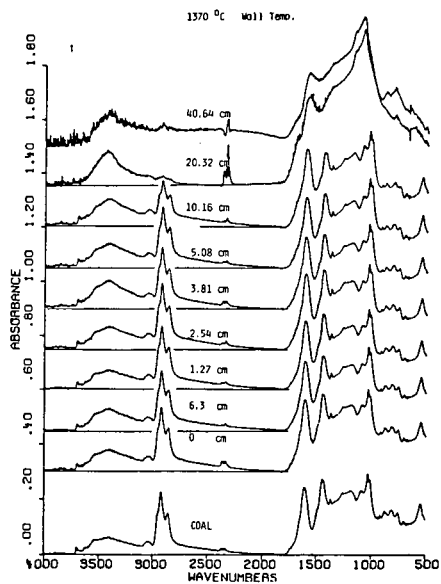
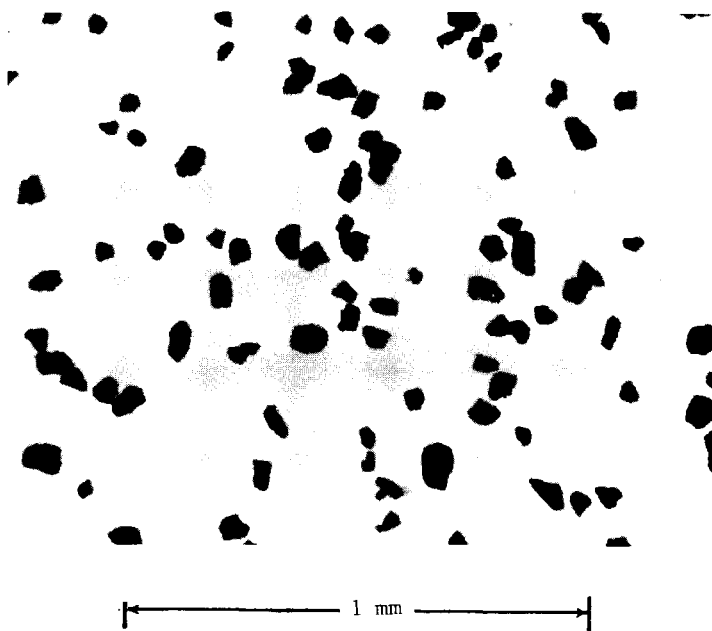


FIGURE 2. INFRARED SPECTRA OF CHARS COLLECTED IN THE DTFS

a), Char Samples at 0 cm.



b). Char Samples at 20 cm.

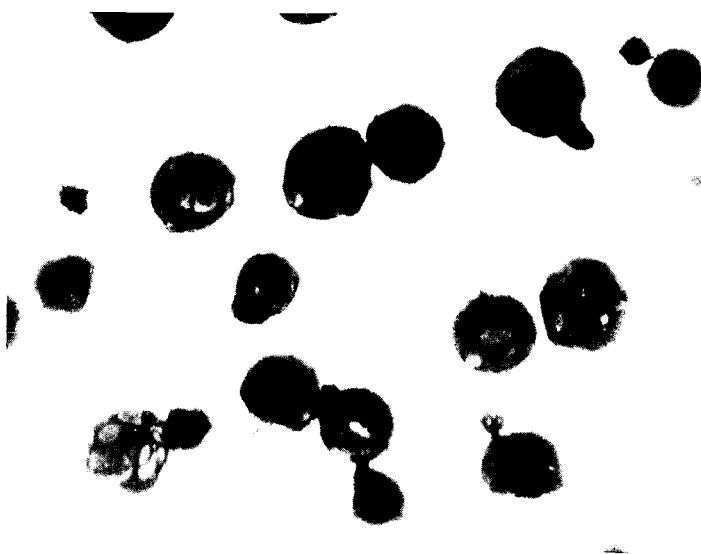


FIGURE 3. PHOTOMICROGRAPHS OF CHAR SAMPLES FROM THE DTFS

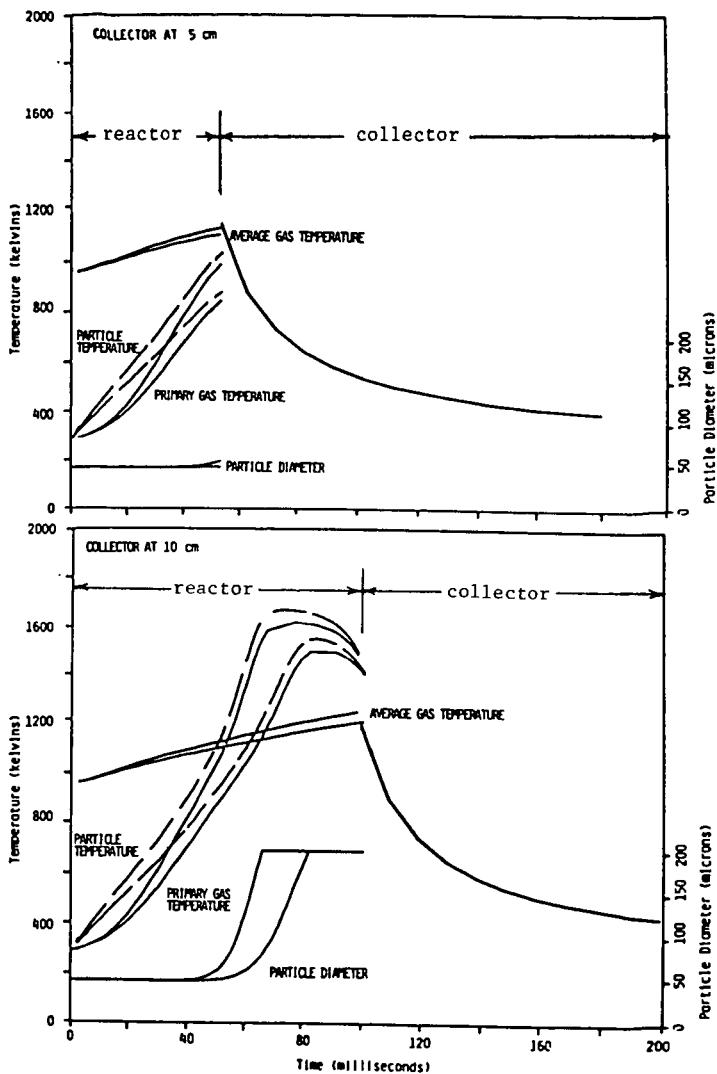
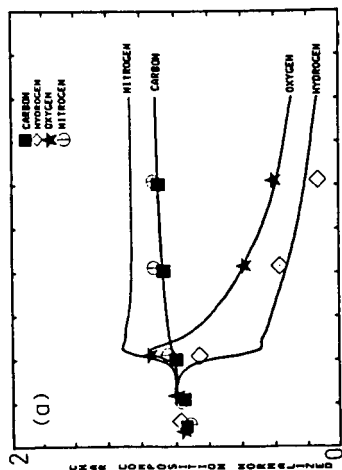


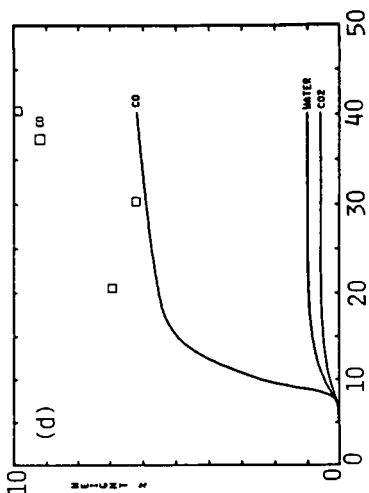
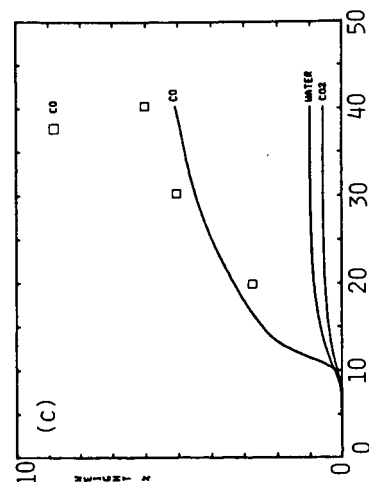
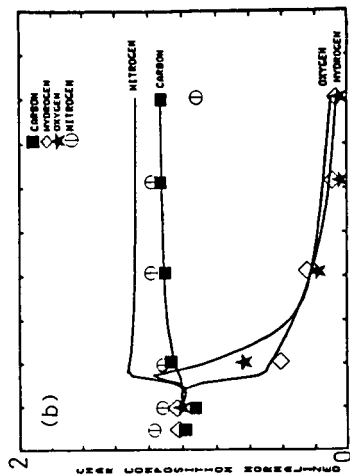
FIGURE 4.

TIME HISTORY OF TEMPERATURE AND PARTICLE DIAMETERS IN THE DTFS. Dashed lines are particle temperatures. Solid lines are the primary gas temperatures, average gas temperatures and particle diameter. A pair of curves is presented for each property. The upper curve is for a 1744 K wall temperature and the lower curve is for 1644 K.

1644K



1744K

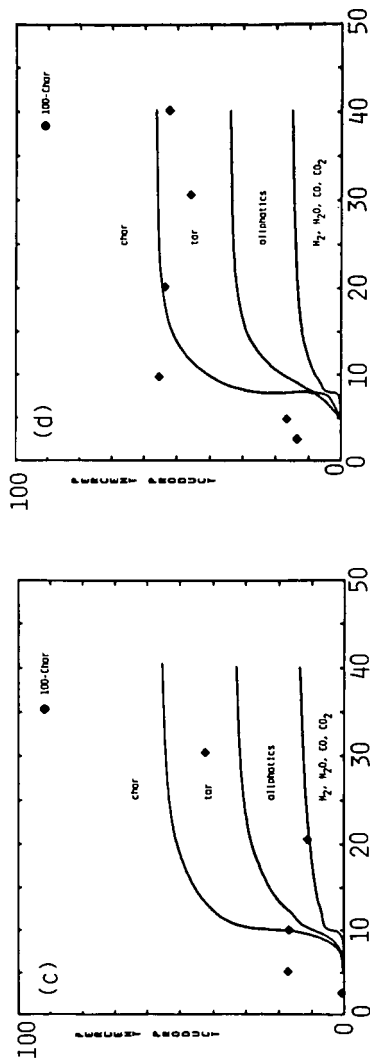
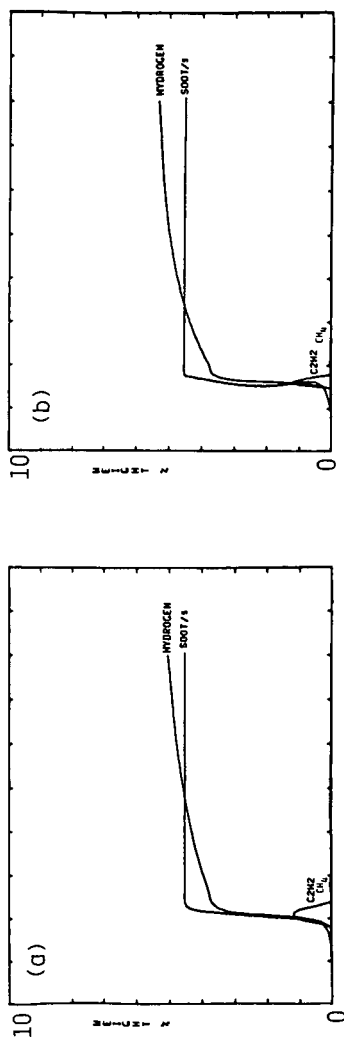


Distance into Reactor (cm)

FIGURE 5. PYROLYSIS PRODUCT DISTRIBUTION. Lines are predictions, symbols are experimental data. In a and b the char composition is normalized by the composition of the parent coal.

1644K

1744K



Distance into Reactor (cm)

FIGURE 6. PYROLYSIS PRODUCT DISTRIBUTION. Lines are predictions, symbols are experimental data. In c and d the symbols are for 100% - % char to correspond to the upper line.